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Preparation of refractory nitride fibers by thermal decomposition of transition metal (Ti, Nb) alkoxide-cellulose precursor gel fibers in NH_3 atmosphere

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Precursor gel fibers have been prepared by extruding cellulose acetate spinning solutions into transition metal (Ti, Nb, Ta) acetone solution as a coagulation bath. Gel formation must be due to the coordination of metal to OH and CO groups on the pyranose ring. The resultant gel fibers have been converted into nitride fibers by pyrolyzing the precursor in NH_3 gas flow at temperatures lower than for powder processing. The precursor gel can give a molecular scale mixture of metal and carbon sources. NbN fiber gave a superconductance at around 13 K. © *2001 Kluwer Academic Publishers*

1. Introduction

SiC fiber is synthesized by pyrolyzing precursor fiber of polycarbosilane and is obtained commercially [1]. However, there are a few studies of the other nitride and carbide inorganic fibers because an appropriate precursor can not be easily obtained. Most transition metals of the forth (Ti, Zr, Hf) and fifth (Nb, Ta) rows of the periodic table form carbide and nitride in these groups with extremely high melting point (3000–4000 °C), excellent high temperature strength, good corrosion and good hardness [2]. However, they cannot be produced as fibers by conventional powder melting of fine powder/polymer composite method. The preparation of TiC fiber has been attempted using an organic compound obtained from the ester exchange reaction of titanium alkoxide and diacetate as a precursor [3]. This precursor is not spinnable because it is insoluble in common solvent and decomposes near its melting point. TiC/C composite fiber can be prepared by pyrolysis of titanium alkoxde-impregnated phenolic resin fiber (Kynol) [4, 5]. There are a few studies of SiC fibers from Kynol fiber impregnated with alkoxide and from activated carbon fiber treated with SiO [6]. TiN and TiC fibers have been prepared by pyrolyzing the sol-gel derived TiO_2 gel precursor fibers in Ar and NH_3 atmosphere, respectively [7, 8]. In a previous paper, we reported that the precursor gel fibers prepared from cellulose and metal alkoxide can be converted into carbite fibers by pyrolyzing the precursor in Ar or N_2 atmosphere [9]. Here, we attempted to prepare nitride fiber by the thermal decomposition of metal (Ti, Nb) cellulose precursor gel fiber in NH_3 atmosphere.

2. Experimental

All chemicals were of the reagent grade commercially available and used without further purificataion. The alkoxides used were titanium tetra-iso-propoxede, niobium penta-n-propoxide and tantalum penta-ethoxide from High Purity Chem. Lab. Cellulose diacetate (acetyl content 39.8%, CA) was purchased from Wako Pure Chemicals. Acetone was dehydrated using a molecular sieve (Nacalai 3A 1/16). X-ray diffraction (XRD) measurements were taken using a Cu K_α with a Ni filter (40 kV, 30 mA). The microstructure of the surface and the cross section of the pyrolyzed fibers were observed by SEM (HITACHI H800) after coating with a thin layer of gold.

Uniform gel fibers were drawn by wet-coagulation spinning method as given in Fig. 1. The 10 wt % CA acetone solution (fiber spinning solution) was slowly fed through the nozzle into the metal alkoxide acetone solution (coagulation bath) by compressed N_2 gas. After standing for 1 hr, the resultant gel fiber was washed with fresh acetone. Gel fibers were dried in air. The precursors were heated up to a given temperature in alumina tube furnace at 600–1400 °C. The heating rate was adjusted to $10\,^\circ\mathrm{C}\cdot\mathrm{min}^{-1}$ and the holding time at the maximum temperature was 1 hour. The SQUID measurements were performed at 10 Gauss in the temperature range of 5–20 K using a superconducting quantum interference device magnetometer.

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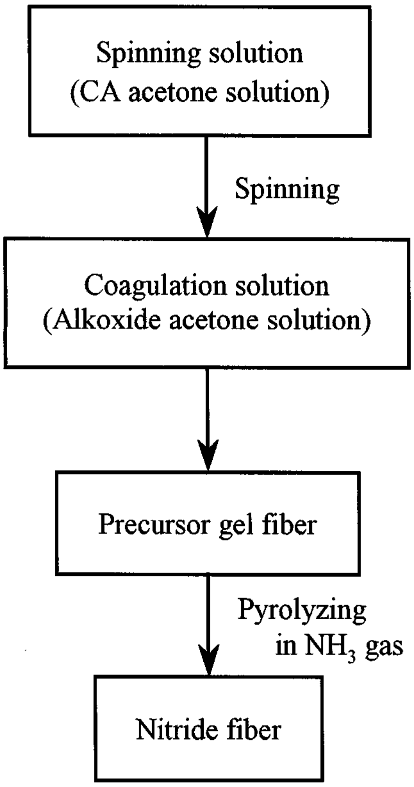

Figure 1 Diagram of nitride fiber preparation process.

3. Results and discussion

When the acetone solution of cellulose derivative is mixed with the acetone solution of the transition polyvalent metal, a transparent gel forms. The gel is elastic and contains 10–20 wt % metal oxide, depending on preparation conditions. It gives no XRD patterns, indicating that it consists of very fine particle or is XRD-amorphous. It can be easily tailored in the forms of fiber, powders, and beads. Gel formation occurs in organic solvents such as DMF, THF, and Dioxane. However, tetra ethoxy silane (TEOS) nor metal acetyl acetonate gave good gel formation. Among cellulose derivative, cellulose diacetate gave good gel.

The sol-gel process with metal alkoxides as precursors has been extensively studied for coating material. Also, this technique allows the preparation of fiber that is difficult to be synthesized by conventional ceramic method. Spinnable viscous sol must be prepared by controlling the hydrolysis and polycondensation reactions of alkoxide. However, continuous spinning is difficult because it needs long period for sol-gel conversion. Our

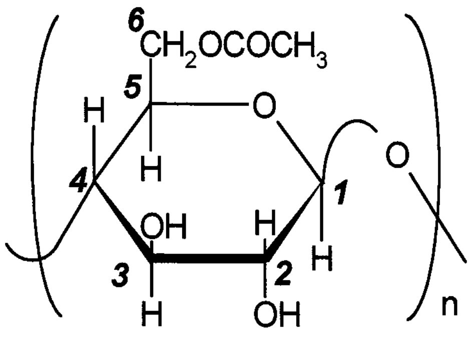

Figure 2 Molecular structure of cellulose acetate (CA).

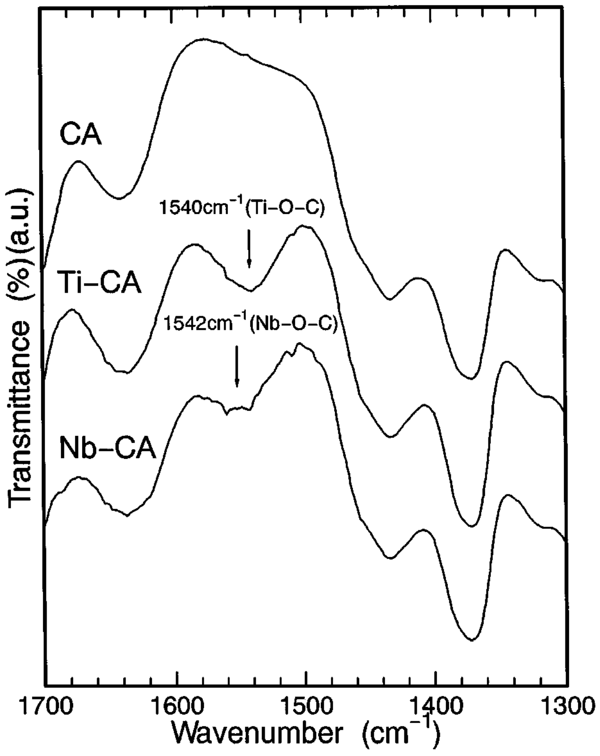

Figure 3 IR spectra of CA and metal (Ti or Nb) alkoxide-CA gel fibers.

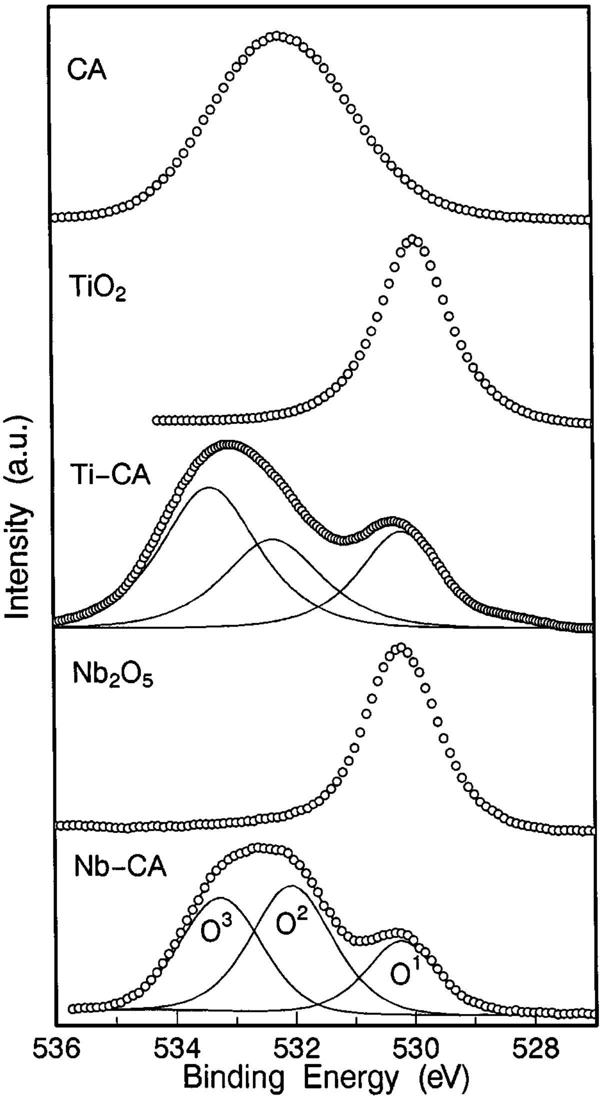

Figure 4 XPS spectra (O1s) of CA, oxide and metal (Ti or Nb) alkoxide-CA gel fibers.

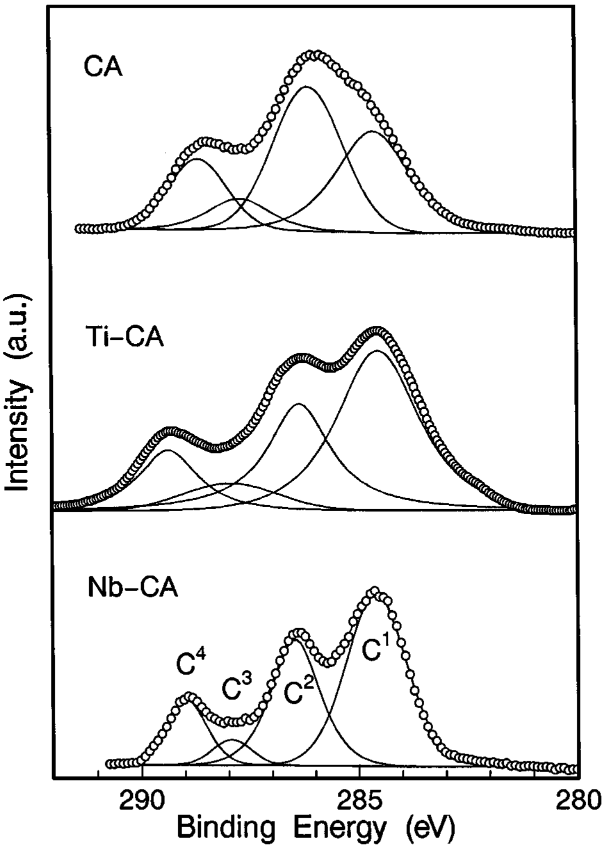

Figure 5 XPS spectra (C1s) of CA and metal (Ti or Nb) alkoxide-CA gel fibers.

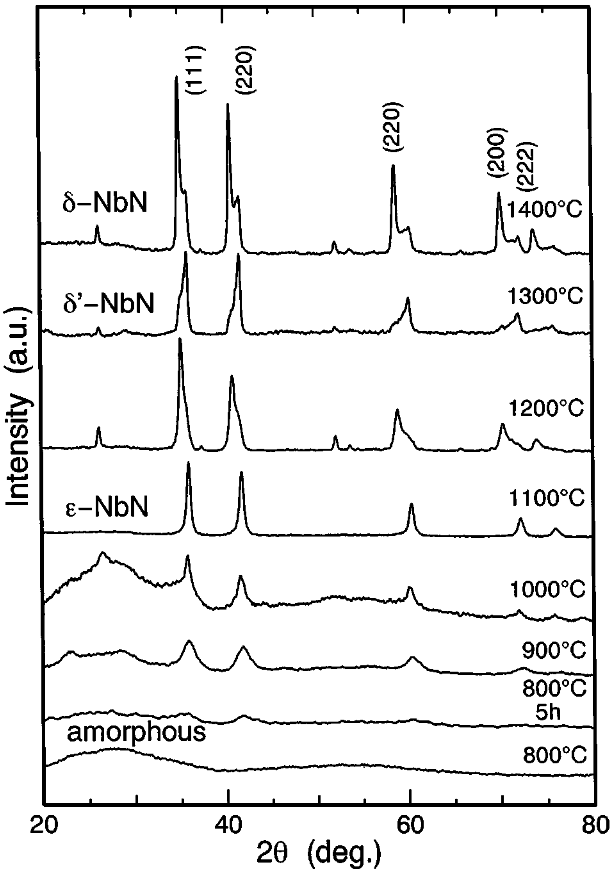

Figure 7 XRD of niobium oxede-CA fiber pyrolyzed at various temperatures in NH_3 gas flow.

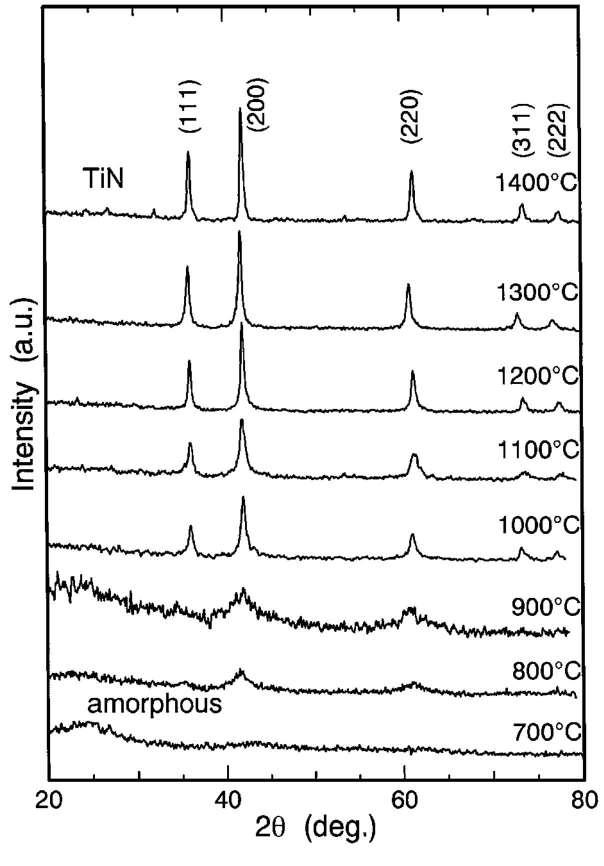

Figure 6 XRD of titanium oxide-CA fiber pyrolyzed at various temperatures in NH_3 gas flow.

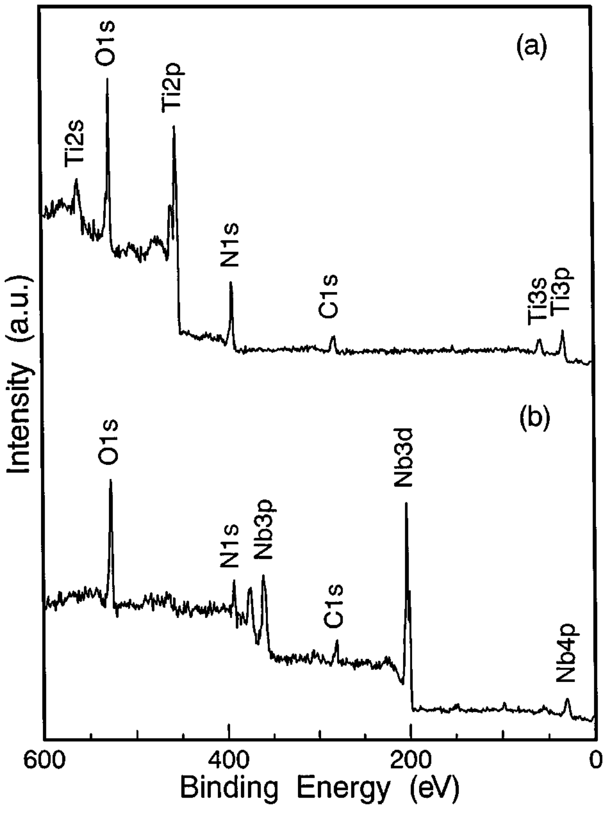

Figure 8 XPS of fibers pyrolyzed in NH_3 gas flow at 1200°C (1 hr). (a) Ti-CA, (b) Nb-CA.

spinning can be continuously performed, similar to conventional wet spinning method. Molecular structure of CA is given in Fig. 2. Numbering denotes position of carbon. Since CA has 39.8% acetyl content, OH groups at C_2 and C_3 are in part acetylyzed. IR spectra are shown in Fig. 3. The bands may be assigned to 3500 cm^{-1} ν_{OH}, 2950–2850 cm^{-1} ν_{CH2}, 1050–1020 cm^{-1} $\delta_{\mathrm{C=O}}$, 1770–1380 cm^{-1} acetate group. New weak bands, 1560 cm^{-1} for CA-Ti, 1540 cm^{-1} for CA-Nb, 1550 cm^{-1} for CA-Ta (not shown) are observed. These are due to the interaction between metal and carbonyl groups. XPS data of O1s for CA, oxide and gel fibers are shown in Fig. 4. Spectra are separated into three peaks [10]. The O^3 may be due to the coordination of metal to OH and CO (acetyl) groups on pyranose ring because O^3 increases with increasing metal oxide. The O^2 is due to non-coordinate O on CA and O^1 is to metal oxide itself. XPS data of C1s for CA and gel fibers are shown in Fig. 5. Spectra are separated into four peaks. The C^1 may be due to the hydrocarbon on CA and alkoxide because C^1 peak emerges largely in gel fiber. The C^2 is to C2–C6 on pyranose ring (shown in Fig. 2) and C^3 to C1 on pyranose ring. The C^4 may be due to acetyl group and it shifts to higher binding energy when gel fiber is formed. In thermal decomposition of CA by N_2 gas, TG curve showed that a marked weight loss occurred at 250–320 °C and subsequently 380–540 °C. The DTA curve indicated that exothermic reaction occurred at 300 °C and then at about 500 °C, corresponding to the above weight loss [9]. The first peak may be due to the decomposition of the side chain and the second to the carbon skeleton. XRD patterns of pulverized fibers are shown in Fig. 6 for titanium oxide-CA and in Fig. 7 for niobium oxide-CA. The pyrolyzed fibers are amorphous until 700 °C for titanium oxide-CA and 800 °C for niobium oxide-CA. However, as shown in the lower of Fig. 7, a longer period of pyrolyzing (5 hr) yields weak pattern. The peaks become sharp with increasing temperature. They show similar patterns because the nitride and carbides both belong to the face-centered cubic structure (NaCl type). Therefore, one cannot distinguish between carbide and nitride from XRD. It was found from XPS that the nitridation of precursor by N_2 hardly occurred at 800°C. As shown in figures, the oxide state is not clearly found and direct nitridation of gel fiber with NH_3 occurs. The phase diagrams for nitrides are incompletely known. NbN species were identified according to literature [2]. The ε phase is described as NbN (I) and the δ phase as NbN (II). The δ' phase (hexagonal) is metastable phase which occurs only during the transition $\delta \rightarrow \varepsilon$. XPS data of pulverized fibers are shown in Fig. 8. The N1s peak indicative of nitride

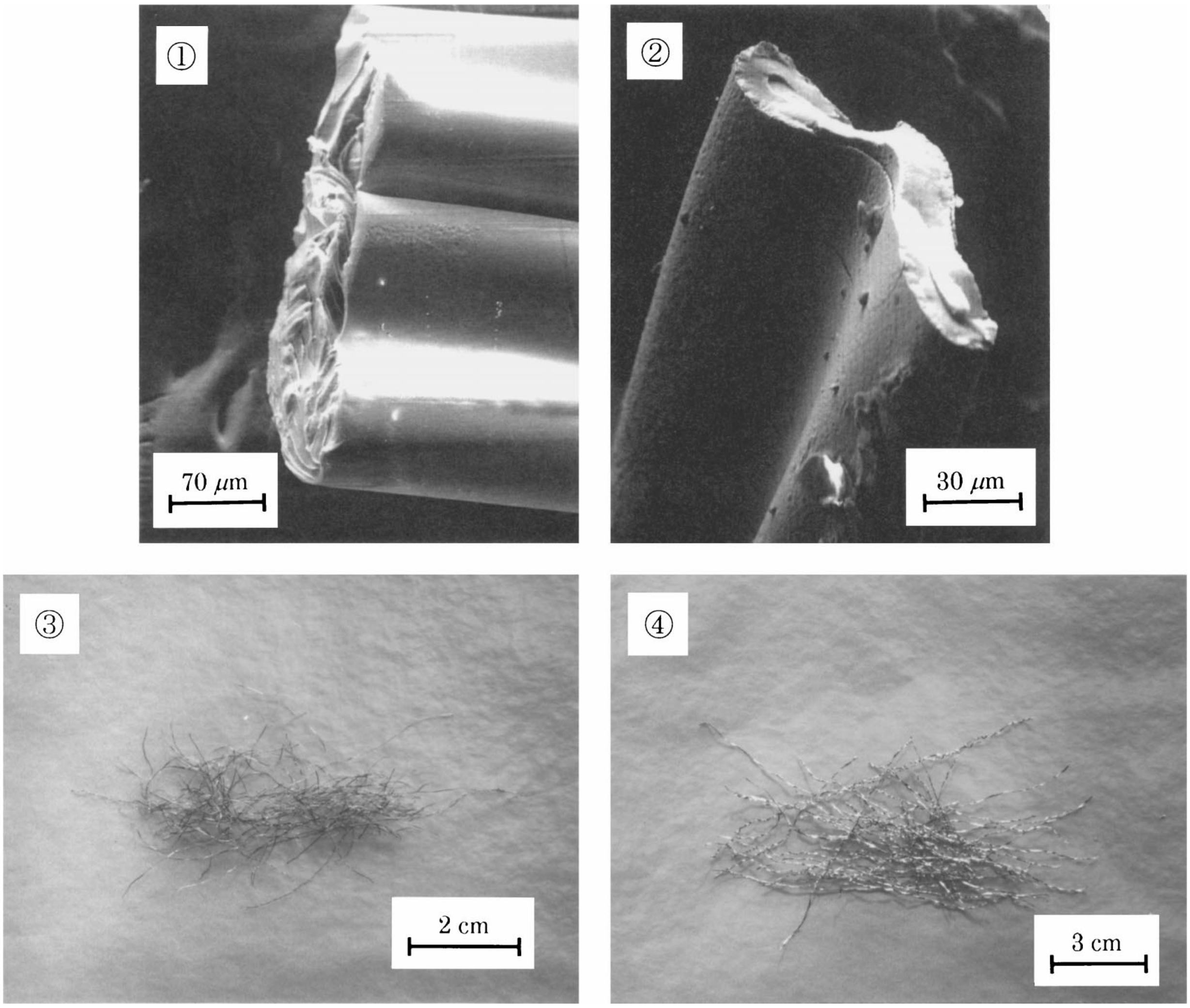

Figure 9 Photograph of fiber and its SEM surface. ① Ti-CA precursor, ② Nb-CA (1200°C), ③ Ti-CA (1200°C), ④ Nb-CA (1000°C).

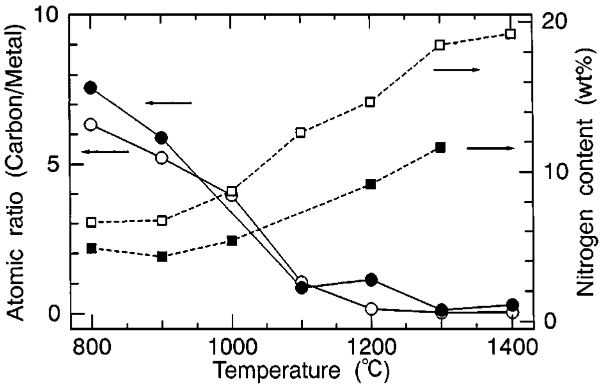

Figure 10 Nitrogen content and atomic ratio (carbon/metal) of fiber pyrolyzed at various temperatures.

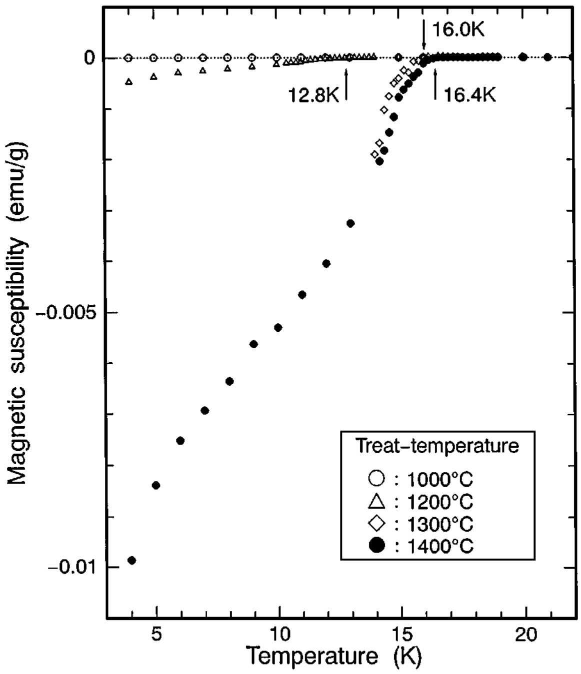

Figure 11 Variations of magnetic susceptibilities for NbN fibers pyrolyzed at differnt temperatures.

is clearly observed. However O1s and C1s peaks are also observed. These indicates the nitride is nonstoichiometric. It is reported that the transition metal carbide and nitride have a tendency to take defect structures (vacancies) and carbon or nitrogen being smaller atoms than the transition metal is always interstitially located [2]. Elemental analysis of fibers pyrolyzed at various temperatures are shown in Fig. 9. With increasing temperature, carbon/metal ratio approaches to zero at about 1200 °C and corresponding to this change, nitrogen contents increases. Amorphous carbon is still residued in fiber pyrolyzed even at 1200 °C. This carbon must act as a reducing agent. Color of fiber changes from gray to gold with increasing temperature. It appears that the nitridation proceeds from fiber surface to its center. Fig. 10 shows a macroscopic view of TiN fiber and a SEM surface. The fibers show golden color. The fiber has no pore and has smooth surface. It is considered that the nitridation proceeds as follows:

$$2TiO_2 + C + 2NH_3 \rightarrow 2TiN + 3H_2O + CO$$

$$Nb_2O_5 + 2C + 2NH_3 \rightarrow 2NbN + 3H_2O + 2CO$$

The Gibbs free energy change ΔG° for the reaction is given using the available thermodynamic data [2]. Reaction will proceed, if the $\Delta G^\circ < 0$. Initial nitridation temperatures calculated from thermodynamics data are 1150 °C for TiN and 1090 °C for NbN. These temperatures are higher than observed temperature 800 °C (as shown in Figs 6 and 7). This denotes that the precursor gel fiber is a molecular scale mixture of metal and carbon sources. The nitrides, in particular, are an interesting class of superconductors. NbN has the higher superconducting critical temperature T_c, critical field and critical current. Fig. 11 shows variations of magnetic susceptibilities with bath temperatures for CA-Nb fibers pyrolyzed at different temperatures. With decreasing temperature, negative magnetic susceptibilities indicative of superconductivity are seen for the fibers pyrolyzed at temperatures higher than 1200 °C. Superconducting transition temperature T_c is defined by a temperature at which magnetic susceptibility changes to minus in sign. T_c values of fibers pyrolyzed at 1200, 1300 and 1400 °C are 12.8, 16.0 and 16.4 K, respectively. With increasing pyrolyzing temperature, the T_c increases and the intensity of negative susceptibilities becomes larger. The T_c obtained here, 16.4 K, exceeds the value 15 K reported in sample prepared by a conventional sintering method [11].

4. Conclusion

Transition metal nitride fibers have been synthesized by thermal conversion of metal alkoxide-cellulose acetate gel fibers prepared by spinning of cellulose solution into alkoxide solution. This method gives the preparation of ceramic fibers that are difficult to synthesize by conventional organic polymer and sol-gel derived precursors. Though not shown, zirconium, hafnium and tantalum nitrides fibers were obtained by this method.

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